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(21)Application number : 09-338371 (71)Applicant : FUJI XEROX CO LTD

(22)Date of filing : 09.12.1997 (72)Inventor : ONO YOSHIYUKI  
IMAI AKIRA  
HIROSE HIDEKAZU  
SATO KATSUHIRO

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(54) OPTICAL SEMICONDUCTOR ELECTRODEPHOTOELECTRIC TRANSDUCERAND  
PHOTOELECTRIC TRANSFER

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an optical semiconductor electrode which is excellent in photoelectric transfer efficiency, stability and durability and can attain easy manufacture by fixing a film including aliphatic hydrocarbon radicals having halogen atoms and pigment having functional groups capable of reacting to the halogen atoms on the surface of the film.

SOLUTION: This electrode involves a semiconductor substrate material, a chemical adsorption film selected from a compound expressed by a formula (I)  $R_1M_1Y_1$  3a, formula (II)  $R_1R_2M_1Y_1$  2a, formula (III)  $R_1R_2R_3M_1Y_1$  and a formula (IV)  $R_1-SH$  (where  $R_1$ : saturated or unsaturated aliphatic hydrocarbon radicals, aromatic hydrocarbon radicals or complex ring radicals including halogen atoms,  $R_2R_3$ : aliphatic hydrocarbon radicals, aromatic hydrocarbon radicals or complex ring radicals in the same radicals, saturated or unsaturated condition as  $R_1M_1$ : 4-valence

element except carbon and Y<sup>1</sup>: hydrolysis functional group) and a pigment expressed by a formula having a functional group which can react to the halogen atoms absorbed in the surface of the chemical adsorption film.

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## CLAIMS

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[Claim(s)]

[Claim 1] An optical semiconductor electrode comprising:

A semiconductor material.

A film chosen from a compound expressed with following formula (I) formed in the surface of this semiconductor material, formula (II), formula (III), and formula (IV) according to a kind at least.

A halogen atom and coloring matter which has a functional group in which a reaction is possible which were fixed to the surface of this film.

formula (I)  $R^1M^1Y^1_3$  type (II)  $R^1R^2M^1Y^1_2$  type (III)  $R^1R^2R^3M^1Y^1$  type (IV)  $R^1-SH$  -- however,  $R^1$  expresses an aliphatic hydrocarbon group of saturation containing at least one halogen atom, or an unsaturation, an aromatic hydrocarbon group, or a heterocycle-containing type group among these formulas.  $R^2$  and  $R^3$  express an aliphatic hydrocarbon group of same basis, saturation, or an unsaturation as  $R^1$ , an aromatic hydrocarbon group, or a heterocycle-containing type group.  $M^1$  expresses tetravalent elements other than carbon.  $Y^1$  is a hydrolytic functional group and expresses a halogen atom or an alkoxy group.

[Claim 2] A halogen atom and the optical semiconductor electrode according to claim 1 in which a functional group in which a reaction is possible is chosen from a carboxyl group and primary amine.

[Claim 3] The optical semiconductor electrode according to claim 1 or 2 in which  $M^1$  is chosen from silicon, germanium, tin, titanium, and a zirconium.

[Claim 4] The optical semiconductor electrode according to any one of claims 1 to 3 in which coloring matter is chosen from a compound expressed with following formula (V), formula (VI), formula (VII), formula (VIII), formula (IX), formula (X), formula (XI), and formula (XII) and which is a kind at least.

Formula (V)

[Formula 1]

In said formula (V),  $R^4$ ,  $R^5$ , and  $R^6$  express a hydrogen atom, a halogen atom,  $-NO_2$ ,  $-OH$ , the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced, or the aromatic hydrocarbon group that may be replaced.  $m$  expresses 1, 2, 3, or 4.  $R^7$  expresses the aliphatic hydrocarbon group of a hydrogen atom or the carbon numbers 1-10.  $Z^1$  expresses a hydrogen atom,  $-NH_2$ ,  $-NHR^8$ ,  $-OH$ , or  $-COOH$ .  $n$  expresses 0, 1, or 2.  $R^8$  expresses the aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced.

Formula (VI)

[Formula 2]

In said formula (VI),  $R^{11}$ ,  $R^{12}$ , and  $R^{13}$  express a hydrogen atom, a halogen atom,  $-NO_2$ ,  $-OH$ , the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced, or the aromatic hydrocarbon group that may be replaced.  $m$  expresses 1 or 2.  $R^{14}$  and  $R^{15}$  express a hydrogen atom, the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced, or the aromatic hydrocarbon group that may be replaced.  $X^{1-}$  expresses a counter ion.  $R^{16}$  expresses the aliphatic hydrocarbon group of a hydrogen atom or the carbon numbers 1-10.  $Z^2$  expresses a hydrogen atom,  $-NH_2$ ,  $-NHR^{17}$ ,  $-OH$ , or  $-COOH$ .  $n$  expresses 0, 1, or 2.  $R^{17}$  expresses the aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. However, when all of  $R^{14}$ ,  $R^{15}$ , and  $R^{16}$  are bases other than a hydrogen atom,  $Z^2$  expresses  $-NH_2$ ,  $-NHR^{17}$ ,  $-OH$ , or  $-COOH$ , and  $n$  expresses 1 or 2.

Formula (VII)

[Formula 3]

In said formula (VII),  $M^2$  expresses Fe, Ru, or Os.  $X^2$  expresses a halogen atom,  $-OH$ ,  $-CN$ , or  $-SCN$ .  $R^{21} - R^{24}$  express a hydrogen atom, a halogen atom,  $-NO_2$ ,  $-COOH$ ,  $-OH$ ,  $-NH_2$ ,  $-NHR^{25}$ , the aliphatic hydrocarbon group of the carbon numbers 1-10, the aromatic hydrocarbon group that may be replaced, or a heterocycle group.  $R^{25}$  expresses the basis, aliphatic hydrocarbon group, or aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. At least one of  $R^{21} - R^{24}$  expresses  $-COOH$ ,  $-OH$ ,  $-NH_2$ ,  $-NHR^{25}$ , or a pyridyl group.

Formula (VIII) [Formula 4]

In said formula (VIII),  $M^3$  expresses Fe, Ru, or Os.  $X^3$  expresses a halogen atom,  $-SO_4$ ,  $-ClO_4$ ,  $-OH$ ,  $-CN$ , or  $-SCN$ .  $n$  expresses 0, 1, or 2.

$R^{31} - R^{36}$  express a hydrogen atom, a halogen atom,  $-NO_2$ ,  $-COOH$ ,  $-OH$ ,  $-NH_2$ ,  $-NHR^8$ , the aliphatic hydrocarbon group of the carbon numbers 1-10, an aromatic hydrocarbon group, or a heterocycle group.  $R^{37}$  expresses the aliphatic hydrocarbon group or aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. At least one of  $R^{31} - R^{36}$  expresses the basis chosen from  $-COOH$ ,  $-OH$ ,  $-NH_2$ ,  $-NHR^{37}$ , or a pyridyl group.

Formula (IX)

[Formula 5]

In said formula (IX),  $M^4$  expresses Fe, Ru, or Os.  $R^{41} - R^{51}$  express a hydrogen atom, a halogen atom,  $-NO_2$ ,  $-COOH$ ,  $-OH$ ,  $-NH_2$ ,  $-NHR^{53}$ , the aliphatic hydrocarbon group of the carbon numbers 1-10, an aromatic hydrocarbon group, or a heterocycle group.  $R^{53}$  expresses the aliphatic hydrocarbon group or aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. At least one of  $R^{41} - R^{51}$  expresses the basis chosen from  $-COOH$ ,  $-OH$ ,  $-NH_2$ ,  $-NHR^{53}$ , or a pyridyl group.

Formula (X)

[Formula 6]

In said formula (X),  $M^5$  expresses  $(H)_2$ , Mg, TiO, VO, Mn, Fe, Co, nickel, Cu, Zn, GaOH, GaCl, InOH, InCl, or SnO.  $R^{61} - R^{64}$  express a hydrogen atom, a halogen atom,  $-NO_2$ ,  $-NH_2$ ,  $-NHR^{65}$ ,  $-OH$ ,  $-COOH$ , the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced, the aromatic hydrocarbon group that may be replaced, or a heterocycle group. At least one of  $R^{61} - R^{64}$  expresses  $-NH_2$ ,  $-NHR^{65}$ ,  $-OH$ , or  $-COOH$ .  $R^{65}$  expresses the aliphatic hydrocarbon group or aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. k, l, m, and n express 1 or 2.

Formula (XI)

[Formula 7]

In said formula (XI),  $M^4$  expresses  $(H)_2$ , Mg, Zn, nickel, Co, Cu, or Pd.  $R^{71} - R^{78}$  express a hydrogen atom, a halogen atom, a hydroxy group, the alkoxy group of the carbon numbers 1-4 which may be replaced, the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced, and the aromatic hydrocarbon group that may be replaced.  $A^1 - A^4$  express the aromatic hydrocarbon group or heterocycle group which may be replaced. At least one of  $A^1 - A^4$  expresses the phenyl group

or pyridyl group replaced by  $\text{-NH}_2$ ,  $\text{-NHR}^{79}$ ,  $\text{-OH}$ , or  $\text{-COOH}$ .  $\text{R}^{79}$  expresses the aliphatic hydrocarbon group or aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced.

Formula (XII)

[Formula 8]

In said formula (XII),  $\text{A}^5$ , - Express an aromatic hydrocarbon group replaced by an aliphatic hydrocarbon group replaced by  $\text{NH}_2$ ,  $\text{-NHR}^{81}$ ,  $\text{-OH}$ ,  $\text{-COOH}$ , or a pyridyl group,  $\text{-NH}_2$ ,  $\text{-NHR}^{81}$ ,  $\text{-OH}$ ,  $\text{-COOH}$ , or a pyridyl group, or a pyridyl group.  $\text{R}^{81}$  expresses an aliphatic hydrocarbon group or an aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced.

[Claim 5]The optical semiconductor electrode according to any one of claims 1 to 4 in which a semiconductor material is chosen from titanium oxide, tin oxide, tungstic oxide, a zinc oxide, indium oxide, niobium oxide, and strontium titanate.

[Claim 6]The optical semiconductor electrode according to any one of claims 1 to 4 whose semiconductor material is titanium oxide.

[Claim 7]A photoelectric conversion device which has a means to connect an electrode of a couple arranged in an electrolytic solution, and an electrode of this couple so that energization is possible, and is characterized by at least one side of the electrodes of this couple being the optical semiconductor electrode according to any one of claims 1 to 6.

[Claim 8]A photoelectric conversion method, wherein it is the photoelectric conversion method of irradiating an electrode of a couple which was mutually connected so that energization was possible, and has been arranged in an electrolytic solution, and producing a photoelectric conversion reaction and at least one side of the electrodes of this couple is the optical semiconductor electrode according to any one of claims 1 to 6.

[Claim 9]A photoelectric conversion method according to claim 8 that a photoelectric conversion reaction is an electrolysis reaction.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]Especially this invention relates light energy

to an optical semiconductor electrode convertible into electrical energy etc., a photoelectric conversion device, and the photoelectric conversion method about an optical semiconductor electrode, a photoelectric conversion device, and the photoelectric conversion method.

[0002]

[Description of the Prior Art] Increase of the global warming by combustion of a fossil fuel and the energy need accompanying the increase in population poses a big problem in connection with human beings' fate. To say nothing of sunlight, since ancient times, the environment of the earth has been cherished till the present and it has become an energy source of all the living things including human beings. These days, it is infinite and using sunlight as a clean energy source which does not generate a toxic substance is examined. As a device which transforms light energy into electrical energy directly, the solar cell in which pn junction was formed on inorganic semiconductors, such as silicon and gallium arsenide, is known well, and it is put in practical use as a power supply of the object for remote places, or a portable electronic device, etc. However, conversion efficiency with these expensive solar cells is acquired. On the other hand, since the energy and cost which manufacture takes are very high, there is a problem that it is difficult to use as an energy resource.

[0003] The wet solar cell using the photoelectrochemical reaction which occurs by the interface of a semiconductor and an electrolytic solution on the other hand considering light energy as an option which changes to electrical energy is known. The titanium oxide used here and an oxide semiconductor like the tin oxide, As compared with semiconductors, such as the above-mentioned silicon and gallium arsenide, far low energy, In titanium oxide and the zinc oxide which can manufacture at cost and are expected especially as a conversion material and which are stable optical semiconductors, the band gap is as large as 3 eV, and since only about 4% of ultraviolet radiation of sunlight can be used, there is a problem that a high energy conversion efficiency cannot be expected.

[0004] On the surface of an optical semiconductor, then, organic coloring matter, such as a xanthene dye and cyanine dye, By using for a photoelectrical pole the modified electrode to which make a small material of band gaps, such as transition metal complexes, such as tris(2,2'-bipyridyl) ruthenium (II), come to stick automatically, it is reported that light energy electrical energy conversion efficiency

may be improved (T. -- Osa, M. Fujihira, *ibid.*, and 264,349 (1976).) Brian O'Regan, Michael Gratzel, *Nature*, 353,736 (1991), JP, 1-220380, A, etc.

[0005] However, in the above electrodes to which make coloring matter come to stick automatically on the surface of an optical semiconductor, chemical stability, electrochemical stability, etc. were insufficient, and in order for the adsorbed coloring matter to tend to \*\*\*\*, there was a problem that a durable field was insufficient.

[0006] The method of fixing coloring matter on the surface of a semiconductor via gamma-aminopropyl triethoxysilane as art which solves many problems in the above former is proposed (JP, 55-124964, A). However, only a little coloring matter can be fixed on the surface of a semiconductor also by this method, but there is a problem that the function as an electrode is not enough.

[0007]

[Problem(s) to be Solved by the Invention] This invention solves many problems in said former, and makes it a technical problem to attain the following purposes. Namely, this invention can absorb sunlight efficiently, can perform energy conversion, is excellent in photoelectric conversion efficiency, stability, and endurance, and aims to let manufacture provide a suitable photoelectric conversion device to enforce the photoelectric conversion method using an easy optical semiconductor electrode and this optical semiconductor electrode, and this photoelectric conversion method.

[0008]

[Means for Solving the Problem] An optical semiconductor electrode which this invention persons absorb sunlight effectively and can transform light energy into electrical energy and chemical energy efficiently, If an optical semiconductor electrode which fixes coloring matter on the surface of a semiconductor with a specific technique is used as a photoelectrical pole as a result of repeating research wholeheartedly about a photoelectric conversion device and a photoelectric conversion method, It found out that could absorb sunlight efficiently, and could perform energy conversion, and this optical semiconductor electrode was excellent in endurance and stability. This invention is based on the above-mentioned knowledge by an artificer of this invention, etc., and said The means for solving a technical problem is as follows. namely [0009] A film chosen from a compound which are following formula (I) formed in the surface of <1> semiconductor material and this semiconductor material, formula (II), formula (III), and formula (IV), and is expressed according to a kind

at least, It is an optical semiconductor electrode which has a halogen atom and coloring matter which has a functional group in which a reaction is possible which were fixed to the surface of this film, and is characterized by things.

formula (I)  $R^1M^1Y^1_3$ , type (II)  $R^1R^2M^1Y^1_2$  type (III)  $R^1R^2R^3M^1Y^1$  type (IV)  $R^1-SH$  -- however,  $R^1$  expresses an aliphatic hydrocarbon group of saturation containing at least one halogen atom, or an unsaturation, an aromatic hydrocarbon group, or a heterocycle-containing type group among these formulas.  $R^2$  and  $R^3$  express an aliphatic hydrocarbon group of same basis, saturation, or an unsaturation as  $R^1$ , an aromatic hydrocarbon group, or a heterocycle-containing type group.  $M^1$  expresses tetravalent elements other than carbon.  $Y^1$  is a hydrolytic functional group and expresses a halogen atom or an alkoxy group.

A functional group in which <2> halogen atoms and a reaction are possible is an optical semiconductor electrode given in the above <1> chosen from a carboxyl group and primary amine.

<3>  $M^1$  is an optical semiconductor electrode given in the above <1> or <2> chosen from silicon, germanium, tin, titanium, and a zirconium.

<4> coloring matter is an optical semiconductor electrode given in either of <3> from the above <1> which is chosen from a compound expressed with following formula (V), formula (VI), formula (VII), formula (VIII), formula (IX), formula (X), formula (XI), and formula (XII) and which is a kind at least.

Formula (V)

[0010]

[Formula 9]

[0011]In said formula (V),  $R^4$ ,  $R^5$ , and  $R^6$  express a hydrogen atom, a halogen atom,  $-NO_2$ ,  $-OH$ , the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced, or the aromatic hydrocarbon group that may be replaced.  $m$  expresses 1, 2, 3, or 4.  $R^7$  expresses the aliphatic hydrocarbon group of a hydrogen atom or the carbon numbers 1-10.  $Z^1$  expresses a hydrogen atom,  $-NH_2$ ,  $-NHR^8$ ,  $-OH$ , or  $-COOH$ .  $n$  expresses 0, 1, or 2.  $R^8$  expresses the aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced.

Formula (VI)

[0012]

[Formula 10]

[0013]In said formula (VI),  $R^{11}$ ,  $R^{12}$ , and  $R^{13}$  express a hydrogen atom, a



halogen atom,  $-\text{NO}_2$ ,  $-\text{OH}$ , an aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced, or an aromatic hydrocarbon group that may be replaced.  $m$  expresses 1 or 2.  $\text{R}^{14}$  and  $\text{R}^{15}$  express a hydrogen atom, an aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced, or an aromatic hydrocarbon group that may be replaced.  $\text{X}^{1-}$  expresses a counter ion.  $\text{R}^{16}$  expresses an aliphatic hydrocarbon group of a hydrogen atom or the carbon numbers 1-10.  $\text{Z}^2$  expresses a hydrogen atom,  $-\text{NH}_2$ ,  $-\text{NHR}^{17}$ ,  $-\text{OH}$ , or  $-\text{COOH}$ .  $n$  expresses 0, 1, or 2.  $\text{R}^{17}$  expresses an aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. However, when all of  $\text{R}^{14}$ ,  $\text{R}^{15}$ , and  $\text{R}^{16}$  are bases other than a hydrogen atom,  $\text{Z}^2$  expresses  $-\text{NH}_2$ ,  $-\text{NHR}^{17}$ ,  $-\text{OH}$ , or  $-\text{COOH}$ , and  $n$  expresses 1 or 2.

Formula (VII)

[0014]

[Formula 11]

[0015] In said formula (VII),  $\text{M}^2$  expresses Fe, Ru, or Os.  $\text{X}^2$  expresses a halogen atom,  $-\text{OH}$ ,  $-\text{CN}$ , or  $-\text{SCN}$ .  $\text{R}^{21} - \text{R}^{24}$  express a hydrogen atom, a halogen atom,  $-\text{NO}_2$ ,  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{NHR}^{25}$ , the aliphatic hydrocarbon group of the carbon numbers 1-10, the aromatic hydrocarbon group that may be replaced, or a heterocycle group.  $\text{R}^{25}$  expresses the basis, aliphatic hydrocarbon group, or aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. At least one of  $\text{R}^{21} - \text{R}^{24}$  expresses  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{NHR}^{25}$ , or a pyridyl group.

Formula (VIII) [0016]

[Formula 12]

[0017] In said formula (VIII),  $\text{M}^3$  expresses Fe, Ru, or Os.  $\text{X}^3$  expresses a halogen atom,  $-\text{SO}_4$ ,  $-\text{ClO}_4$ ,  $-\text{OH}$ ,  $-\text{CN}$ , or  $-\text{SCN}$ .  $n$  expresses 0, 1, or 2.  $\text{R}^{31} - \text{R}^{36}$  express a hydrogen atom, a halogen atom,  $-\text{NO}_2$ ,  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{NHR}^8$ , an aliphatic hydrocarbon group of the carbon numbers 1-10, an aromatic hydrocarbon group, or a heterocycle group.  $\text{R}^{37}$  expresses an aliphatic hydrocarbon group or an aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. At least one of  $\text{R}^{31} - \text{R}^{36}$  expresses a basis chosen from  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{NHR}^{37}$ , or a pyridyl group.

Formula (IX)

[0018]

[Formula 13]

[0019]In said formula (IX),  $M^4$  expresses Fe, Ru, or Os.  $R^{41} - R^{51}$  express a hydrogen atom, a halogen atom,  $-NO_2$ ,  $-COOH$ ,  $-OH$ ,  $-NH_2$ ,  $-NHR^{53}$ , the aliphatic hydrocarbon group of the carbon numbers 1-10, an aromatic hydrocarbon group, or a heterocycle group.  $R^{53}$  expresses the aliphatic hydrocarbon group or aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. At least one of  $R^{41} - R^{51}$  expresses the basis chosen from  $-COOH$ ,  $-OH$ ,  $-NH_2$ ,  $-NHR^{53}$ , or a pyridyl group.

Formula (X)

[0020]

[Formula 14]

[0021]In said formula (X),  $M^5$  expresses  $(H)_2$ , Mg, TiO, VO, Mn, Fe, Co, nickel, Cu, Zn, GaOH, GaCl, InOH, InCl, or SnO.  $R^{61} - R^{64}$  express a hydrogen atom, a halogen atom,  $-NO_2$ ,  $-NH_2$ ,  $-NHR^{65}$ ,  $-OH$ ,  $-COOH$ , the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced, the aromatic hydrocarbon group that may be replaced, or a heterocycle group. At least one of  $R^{61} - R^{64}$  expresses  $-NH_2$ ,  $-NHR^{65}$ ,  $-OH$ , or  $-COOH$ .  $R^{65}$  expresses the aliphatic hydrocarbon group or aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. k, l, m, and n express 1 or 2.

Formula (XI)

[0022]

[Formula 15]

[0023]In said formula (XI),  $M^4$  expresses  $(H)_2$ , Mg, Zn, nickel, Co, Cu, or Pd.  $R^{71} - R^{78}$  express a hydrogen atom, a halogen atom, a hydroxy group, the alkoxy group of the carbon numbers 1-4 which may be replaced, the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced, and the aromatic hydrocarbon group that may be replaced.  $A^1 - A^4$  express the aromatic hydrocarbon group or heterocycle group which may be replaced. At least one of  $A^1 - A^4$  expresses the phenyl group or pyridyl group replaced by  $-NH_2$ ,  $-NHR^{79}$ ,  $-OH$ , or  $-COOH$ .  $R^{79}$  expresses the aliphatic hydrocarbon group or aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced.

Formula (XII)

[0024]

[Formula 16]

[0025]In said formula (XII), A<sup>5</sup>, - Express an aromatic hydrocarbon group replaced by an aliphatic hydrocarbon group replaced by NH<sub>2</sub>, -NHR<sup>81</sup>, -OH, -COOH, or a pyridyl group, -NH<sub>2</sub>, -NHR<sup>81</sup>, -OH, -COOH, or a pyridyl group, or a pyridyl group. R<sup>81</sup> expresses an aliphatic hydrocarbon group or an aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced.

[0026]<5> semiconductor materials are optical semiconductor electrodes given in either of <4> from the above <1> chosen from titanium oxide, tin oxide, tungstic oxide, a zinc oxide, indium oxide, niobium oxide, and strontium titanate.

<6> semiconductor materials are optical semiconductor electrodes given in either of <4> from the above <1> which is titanium oxide.

It has a means to connect an electrode of a couple arranged in <7> electrolytic solutions, and an electrode of this couple so that energization is possible, and at least one side of the electrodes of this couple is a photoelectric conversion device characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <6>.

<8> It is the photoelectric conversion method of irradiating an electrode of a couple which was mutually connected so that energization was possible, and has been arranged in an electrolytic solution, and producing a photoelectric conversion reaction, At least one side of the electrodes of this couple is the photoelectric conversion method characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <6>.

<Nine> photoelectric conversion reactions are the photoelectric conversion methods given in the above <8> which is an electrolysis reaction.

[0027]

[Embodiment of the Invention]Hereafter, it explains to details per the optical semiconductor electrode of this invention, a photoelectric conversion device, and photoelectric conversion method.

[0028](Optical semiconductor electrode) This invention is characterized by an optical semiconductor electrode comprising the following.

Semiconductor material.

The film formed in the surface of this semiconductor material.

Coloring matter fixed to the surface of this film.

[0029]- Semiconductor material - There is no restriction in particular about the shape of said semiconductor material, structure, and a size,

and it can choose suitably according to the purpose. Said semiconductor material is used as a substrate. As said substrate, it may be a substrate which consists only of semiconductor materials, for example, and may be a substrate which forms the coating membrane by a semiconductor material on substrates by a suitably selected material, such as glass. As said semiconductor material, there is no restriction in particular and it can choose from an n-type semiconductor, a p-type semiconductor, etc. suitably according to the purpose.

[0030]As an n-type semiconductor, titanium oxide, a cadmium sulfide, strontium titanate, tungstic oxide, a zinc oxide, indium oxide, niobium oxide, tin oxide, molybdenum disulfide, etc. are mentioned, for example. As a p-type semiconductor, gallium phosphide, gallium arsenide, indium phosphide, etc. are mentioned, for example. Also in these, titanium oxide, the tin oxide, tungstic oxide, a zinc oxide, indium oxide, niobium oxide, and strontium titanate are preferred in respect of the characteristic, chemical stability, and manufacturability, and especially titanium oxide is preferred.

[0031]- Film - Said film is a chemical adsorption film (a chemical-absorption monomolecular film or a chemical-absorption built up film) chosen from the compound expressed with following formula (I), formula (II), formula (III), and formula (IV) according to a kind at least. formula (I)  $R^1M^1Y^1_3$  type (II)  $R^1R^2M^1Y^1_2$  type (III)  $R^1R^2R^3M^1Y^1$  type (IV)  $R^1-SH$  -- however,  $R^1$  expresses the aliphatic hydrocarbon group of the saturation containing at least one halogen atom, or an unsaturation, an aromatic hydrocarbon group, or a heterocycle-containing type group among these formulas.  $R^2$  and  $R^3$  express the aliphatic hydrocarbon group of the same basis, saturation, or unsaturation as  $R^1$ , an aromatic hydrocarbon group, or a heterocycle-containing type group.  $M^1$  expresses tetravalent elements other than carbon.  $Y^1$  is a hydrolytic functional group and expresses a halogen atom or an alkoxy group.

[0032]Said film makes a kind react that it is few as being chosen as said semiconductor material from the compound expressed with said formula (I) which has a halogen atom which is a weak reaction group of an interaction with this semiconductor material, formula (II), formula (III), and formula (IV), and is formed in the surface of this semiconductor material.

[0033]As an example of a compound expressed with said formula (I) - (IV), p-bromophenyltrichlorosilane [ $p-BrPhSiCl_3$ ], p-bromo phenyltrimethoxysilane [ $p-BrPhSi(OCH_3)_3$ ], o-bromophenyltrichlorosilane [ $o-BrPhSiCl_3$ ], o-bromo phenyltrimethoxysilane [ $o-BrPhSi(OCH_3)_3$ ], m-bromophenyltrichlorosilane [ $m-BrPhSiCl_3$ ], m-bromo phenyltrimethoxysilane [ $m-BrPhSi(OCH_3)_3$ ], (p-bromomethyl)

Phenyltrichlorosilane [ $p\text{-BrCH}_2\text{PhSiCl}_3$ ], (p-bromomethyl)  
 Phenyltrimethoxysilane [ $p\text{-BrCH}_2\text{PhSi}(\text{OCH}_3)_3$ ], Bromomethyl  
 trichlorosilane [ $\text{BrCH}_2\text{SiCl}_3$ ], bromomethyl trichloro germane  
 [ $\text{BrCH}_2\text{GeCl}_3$ ], bromomethyl trimethoxysilane [ $\text{BrCH}_2\text{Si}(\text{OCH}_3)_3$ ],  
 Bromomethyl trimethoxy germane [ $\text{BrCH}_2\text{germanium}(\text{OCH}_3)_3$ ], Bromomethyl  
 triethoxysilane [ $\text{BrCH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ], Bromomethyl dimethylchlorosilicane  
 [ $\text{BrCH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ ] bromomethyl dimethylchloro germane  
 [ $\text{BrCH}_2\text{germanium}(\text{CH}_3)_2\text{Cl}$ ], [0034]2-bromoethyltrichlorosilane  
 [ $\text{CH}_3\text{CHBrSiCl}_3$ ], 2-bromoethyltrichloro germane [ $\text{CH}_3\text{CHBrGeCl}_3$ ], 1.2-  
 dibromoethyltrichlorosilane [ $\text{BrCH}_2\text{CHBrSiCl}_3$ ], 1.2-dibromoethyltrichloro  
 germane [ $\text{BrCH}_2\text{CHBrGeCl}_3$ ], 3-bromopropyl trichloro germane [ $\text{Br}(\text{CH}_2)_3\text{GeCl}_3$ ],  
 4-bromo butyldimethyl chlorosilicane [ $\text{Br}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{Cl}$ ],  
 3-bromopropyl trichlorosilane [ $\text{Br}(\text{CH}_2)_3\text{SiCl}_3$ ], 3-bromopropyl  
 trimethoxysilane [ $\text{Br}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ ], 3-bromopropyl triethoxysilane  
 [ $\text{Br}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ] 8-bromooctyltrichlorosilane [ $\text{Br}(\text{CH}_2)_8\text{SiCl}_3$ ], 8-  
 bromooctyl trimethoxysilane [ $\text{Br}(\text{CH}_2)_8\text{Si}(\text{OCH}_3)_3$ ], 8-bromooctyl  
 triethoxysilane [ $\text{Br}(\text{CH}_2)_8\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ], 8-  
 bromooctyldimethylchlorosilicane [ $\text{Br}(\text{CH}_2)_8\text{Si}(\text{CH}_3)_2\text{Cl}$ ], 11-  
 bromoundecyltrichlorosilane [ $\text{Br}(\text{CH}_2)_{11}\text{SiCl}_3$ ], 11-bromoundecyl  
 trimethoxysilane [ $\text{Br}(\text{CH}_2)_{11}\text{Si}(\text{OCH}_3)_3$ ], 11-bromoundecyl triethoxysilane  
 [ $\text{Br}(\text{CH}_2)_{11}\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ], 3-bromopropyl trichloro germane [ $\text{Br}(\text{CH}_2)_3\text{GeCl}_3$ ],  
 bromomethyl tribromo germane [ $\text{BrCH}_2\text{GeBr}_3$ ], [0035]p-chlorophenyl  
 trichlorosilane [ $p\text{-ClPhSiCl}_3$ ], p-chlorophenyl trimethoxysilane [ $p\text{-ClPhSi}(\text{OCH}_3)_3$ ],  
 m-chlorophenyl trichlorosilane [ $m\text{-ClPhSiCl}_3$ ], o-  
 chlorophenyl trimethoxysilane [ $o\text{-ClPhSi}(\text{OCH}_3)_3$ ], (p-chloromethyl)  
 Phenyltrichlorosilane [ $p\text{-ClCH}_2\text{PhSiCl}_3$ ], (p-chloromethyl)  
 Phenyltrimethoxysilane [ $p\text{-ClCH}_2\text{PhSi}(\text{OCH}_3)_3$ ], (p-chloromethyl)  
 Phenylmethyl dichlorosilane [ $p\text{-ClCH}_2\text{PhSi}(\text{CH}_3)_2\text{Cl}_2$ ], (p-chloromethyl)  
 Phenyldimethylchlorosilicane [ $p\text{-ClCH}_2\text{PhSi}(\text{CH}_3)_2\text{Cl}$ ], (p-chloromethyl)  
 FENIRUTORI n-propoxysilane [ $p\text{-ClCH}_2\text{PhSi}(\text{O-n-C}_3\text{H}_7)_3$ ], (p-chloromethyl)  
 Trichlorosilane [ $p\text{-ClCH}_2\text{Ph}(\text{CH}_2)_2\text{SiCl}_3$ ] (phenylethyl), (p-chloromethyl)  
 Methyl di chlorosilicane [ $p\text{-ClCH}_2\text{Ph}(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2\text{Cl}_2$ ] (phenylethyl), (p-  
 chloromethyl) Dimethylchlorosilicane [ $p\text{-ClCH}_2\text{Ph}(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2\text{Cl}$ ]  
 (phenylethyl), (p-chloromethyl) Trimethoxysilane [ $p\text{-ClCH}_2\text{Ph}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ ]  
 (phenylethyl), (m-chloromethyl) Trichlorosilane [ $m\text{-ClCH}_2\text{Ph}(\text{CH}_2)_2\text{SiCl}_3$ ]  
 (phenylethyl), (m-chloromethyl) Methyl di  
 chlorosilicane [ $m\text{-ClCH}_2\text{Ph}(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2\text{Cl}_2$ ] (phenylethyl), (m-  
 chloromethyl) Dimethylchlorosilicane [ $m\text{-ClCH}_2\text{Ph}(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2\text{Cl}$ ]  
 (phenylethyl), (m-chloromethyl) Trimethoxysilane [ $m\text{-ClCH}_2\text{Ph}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ ]  
 (phenylethyl), (o-chloromethyl) Trichlorosilane [ $o\text{-ClCH}_2\text{Ph}(\text{CH}_2)_2\text{SiCl}_3$ ]  
 (phenylethyl), (o-chloromethyl) Methyl di  
 chlorosilicane [ $o\text{-ClCH}_2\text{Ph}(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2\text{Cl}_2$ ] (phenylethyl), (o-

chloromethyl) Dimethylchlorosilicane [ $\text{o-ClCH}_2\text{Ph}(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2\text{Cl}$ ]  
 (phenylethyl), (o-chloromethyl) Trimethoxysilane (phenylethyl) [ $\text{o-ClCH}_2\text{Ph}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ ], [0036]Chloromethyl trichlorosilane  
 $[\text{Cl}_3\text{CSiCl}_3]$ , Trichloromethyl trichlorosilane [ $\text{ClCH}_2\text{SiCl}_3$ ],  
 Trichloromethyl trichloro germane [ $\text{ClCH}_2\text{GeCl}_3$ ], Chloromethyl  
 trimethoxysilane [ $\text{ClCH}_2\text{Si}(\text{OCH}_3)_3$ ], Chloromethyl triethoxysilane  
 $[\text{ClCH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3]$ , Chloromethyl trimethoxy germane  
 $[\text{ClCH}_2\text{germanium}(\text{OCH}_3)_3]$ , Chloromethyl dimethylchlorosilicane  
 $[\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{Cl}]$ , Chloromethyl methyldi chlorosilicane [ $\text{ClCH}_2\text{Si}(\text{CH}_3)\text{Cl}_2$ ],  
 Chloromethyl methyldiethoxysilane [ $\text{ClCH}_2\text{Si}(\text{CH}_3)(\text{OCH}_2\text{CH}_3)_2$ ],  
 Chloromethyl methyldi isopropoxysilane [ $\text{ClCH}_2\text{Si}(\text{CH}_3)(\text{OCH}(\text{CH}_3)_2)_2$ ],  
 Bis(chloromethyl)dichlorosilane [ $(\text{ClCH}_2)_2\text{SiCl}_2$ ],  
 Bis(chloromethyl)methylchlorosilicane [ $(\text{ClCH}_2)_2\text{SiCH}_3\text{Cl}$ ], 1-  
 chloroethyltrichlorosilane [ $\text{ClCHCH}_3\text{SiCl}_3$ ], 1,2-  
 dichloroethyltrichlorosilane [ $\text{CH}_2\text{ClCHClSiCl}_3$ ], (Dichloromethyl)  
 Trichlorosilane [ $\text{CHCl}_2\text{SiCl}_3$ ], (Dichloromethyl) Methyldi chlorosilicane  
 $[\text{CHCl}_2\text{Si}(\text{CH}_3)\text{Cl}_2]$ , (Dichloromethyl) Dimethylchlorosilicane  
 $[\text{CHCl}_2\text{Si}(\text{CH}_3)_2\text{Cl}]$ , 2-chloroethyltrichlorosilane [ $\text{Cl}(\text{CH}_2)_2\text{SiCl}_3$ ], 2-  
 chloro ethyltriethoxysilane [ $\text{Cl}(\text{CH}_2)_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ] 2-chloroethyl  
 methyldi chlorosilicane [ $\text{Cl}(\text{CH}_2)_2\text{SiCl}_2\text{CH}_3$ ], 2-chloroethyl methyl  
 dimethoxysilane [ $\text{Cl}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_2\text{CH}_3$ ], 2-(chloromethyl)  
 allyltrichlorosilane [ $\text{CH}_2=\text{C}(\text{CH}_2\text{Cl})\text{SiCl}_3$ ], 1-(chloromethyl)  
 allyltrichlorosilane [ $\text{CH}(\text{CH}_2\text{Cl})=\text{CH}_2\text{SiCl}_3$ ], 3-chloropropyl  
 trichlorosilane [ $\text{Cl}(\text{CH}_2)_3\text{SiCl}_3$ ], 3-chloropropyl trichloro germane  
 $[\text{Cl}(\text{CH}_2)_3\text{GeCl}_3]$ , 3-chloropropyl dimethylchlorosilicane [ $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{Cl}$ ],  
 3-chloropropyl dimethyl germane [ $\text{Cl}(\text{CH}_2)_3\text{germanium}(\text{CH}_3)_2\text{Cl}$ ],  
 3-chloropropyl methyldi chlorosilicane [ $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{CH}_3)\text{Cl}_2$ ] 3-  
 chloropropyl phenyl dichlorosilane [ $\text{Cl}(\text{CH}_2)_3\text{SiPhCl}_2$ ], 3-chloropropyl  
 dimethyl methoxysilane [ $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2(\text{OCH}_3)$ ], 3-  
 chloropropyltrimetoxysilane [ $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ ], 3-chloropropyl  
 triethoxysilane [ $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ], 3-  
 chloropropylmethyldimethoxysilane [ $\text{Cl}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2$ ], 3-  
 chloropropyl methyldiethoxysilane [ $\text{Cl}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_2\text{CH}_3)_2$ ], 4-  
 chlorobutyl dimethylchlorosilicane [ $\text{Cl}(\text{CH}_2)_4\text{SiCl}(\text{CH}_3)_2$ ], 8-  
 chlorooctyltrichlorosilane [ $\text{Cl}(\text{CH}_2)_8\text{SiCl}_3$ ] 8-chlorooctyl  
 trimethoxysilane [ $\text{Cl}(\text{CH}_2)_8\text{Si}(\text{OCH}_3)_3$ ], 8-chlorooctyl triethoxysilane  
 $[\text{Cl}(\text{CH}_2)_8\text{Si}(\text{OCH}_2\text{CH}_3)_3]$ , [0037]p-iodophenyltrichlorosilane [ $\text{p-IPhSiCl}_3$ ],  
 p-iodo phenyltrimethoxysilane [ $\text{p-IPhSi}(\text{OCH}_3)_3$ ], (p-iodomethyl)  
 Phenyltrichlorosilane [ $\text{p-ICH}_2\text{PhSiCl}_3$ ], (p-iodomethyl)  
 Phenyltrimethoxysilane [ $\text{p-ICH}_2\text{PhSi}(\text{OCH}_3)_3$ ], Iodomethyltrichlorosilane  
 $[\text{ICH}_2\text{SiCl}_3]$ , Iodo methyl trimetoxysilane [ $\text{ICH}_2\text{Si}(\text{OCH}_3)_3$ ], Iodomethyl  
 triethoxysilane [ $\text{ICH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ], 3-iodopropyltrichlorosilane [ $\text{I}(\text{CH}_2)_3\text{SiCl}_3$ ]

$\text{SiCl}_3$ ], 3-iodo propyltrimethoxysilane  $[\text{I}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]$  3-iodopropyl triethoxysilane  $[\text{I}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3]$ , 8-iodooctyltrichlorosilane  $[\text{I}(\text{CH}_2)_8\text{SiCl}_3]$ , 8-iodooctyl trimethoxysilane  $[\text{I}(\text{CH}_2)_8\text{Si}(\text{OCH}_3)_3]$  8-iodooctyl triethoxysilane  $[\text{I}(\text{CH}_2)_8\text{Si}(\text{OCH}_2\text{CH}_3)_3]$ , [0038] (3-glycidoxy propyl) Trimethoxysilane  $[\text{CH}_2\text{OCHCH}_2\text{-O-}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]$ , Acetoxyethyltrichlorosilane  $[\text{CH}_3\text{COOCH}_2\text{CH}_2\text{SiCl}_3]$ , Acetoxy ethyltriethoxysilane  $[\text{CH}_3\text{COOCH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3]$ , Acetoxy ethyltrimethoxysilane  $[\text{CH}_3\text{COOCH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3]$ , 3-bromopropyl thiol  $[\text{Br}(\text{CH}_2)_3\text{SH}]$ , 8-bromooctyl thiol  $[\text{Br}(\text{CH}_2)_8\text{SH}]$ , 8-bromoundecyl thiol  $[\text{Br}(\text{CH}_2)_{11}\text{SH}]$ , p -- a - bromophenyl thiol o[  $[\text{p-BrPhSH}]$  ]-bromophenyl thiol  $[\text{o-BrPhSH}]$  m-bromophenyl thiol  $[\text{m-BrPhSH}]$  and a phenyl (p-bromomethyl) thiol  $[\text{p-BrCH}_2\text{PhSH}]$ . 3-chloropropyl thiol  $[\text{Cl}(\text{CH}_2)_3\text{SH}]$ , 8-chlorooctyl thiol  $[\text{Cl}(\text{CH}_2)_8\text{SH}]$ , A p-chlorophenyl thiol  $[\text{p-ClPhSH}]$  o-chlorophenyl thiol  $[\text{o-ClPhSH}]$ , m-chlorophenyl thiol  $[\text{m-ClPhSH}]$ , a phenyl (p-chloromethyl) thiol  $[\text{p-ClCH}_2\text{PhSH}]$ , 3-iodopropyl thiol  $[\text{I}(\text{CH}_2)_3\text{SH}]$ , 8 -- a - iodooctyl thiol p[  $[\text{I}(\text{CH}_2)_8\text{SH}]$  ]-iodophenyl thiol  $[\text{o-IPhSH}]$  m-iodophenyl thiol  $[\text{m-IPhSH}]$ , a phenyl (p-iodomethyl) thiol  $[\text{p-ICH}_2\text{PhSH}]$ , etc. are mentioned. "Ph" expresses a phenyl group or a phenylene group among these formulas. These compounds may be used by an one-sort independent, and may use two or more sorts together.

[0039] A silane compound is preferred in respect of composition being easy, a kind being abundant also in these compounds, reactivity being high, and the intensity of combination being high etc. In the case of the thing applicable to the compound expressed with said formula (I), three  $\text{Y}^1$ , When  $\text{R}^2$  is the same as  $\text{R}^1$ , by corresponding to the compound which is said formula (II) and is expressed two  $\text{Y}^1$  and  $\text{R}^2$ , And when  $\text{R}^2$  and  $\text{R}^3$  are the same as  $\text{R}^1$ , by corresponding to the compound which is said (III) and is expressed  $\text{Y}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$ , Since it reacts to the hydroxyl group in the surface of said semiconductor base material, etc., respectively and a covalent bond is formed, associative strength with said semiconductor material per molecule of this compound is firmer.

[0040] Also in these compounds, correspond to said formula (II) and  $\text{R}^2$  The saturation of the carbon numbers 1-20 or an unsaturation, In the case of what is an aliphatic hydrocarbon group, an aromatic hydrocarbon group, or a heterocycle-containing type group,  $\text{Y}^1$  and  $\text{R}^2$ , Correspond to said (III) and  $\text{R}^2$  and  $\text{R}^3$  And the saturation of the carbon numbers 1-20 or an unsaturation, Since in the case of what is an aliphatic hydrocarbon group, an aromatic hydrocarbon group, or a heterocycle-containing type group only  $\text{Y}^1$  reacts to the hydroxyl group in the surface of said semiconductor material, etc., respectively and a covalent bond is formed, lessening the number of combination with

said semiconductor material per molecule of an above-mentioned compound -- things are made and many above-mentioned compounds can be introduced more into the surface of said semiconductor material.

[0041]- Coloring matter - Said coloring matter has at least one functional group in which a halogen atom and a reaction are possible, As being suitably chosen from the compound which shows sensitization and should just be expressed with following formula (V), formula (VI), formula (VII), formula (VIII), formula (IX), formula (X), formula (XI), and formula (XII), it is a kind as it is few. Said coloring matter is fixed to the surface of said film.

[0042]Formula (V)

[0043]

[Formula 17]

[0044]In said formula (V),  $R^4$ ,  $R^5$ , and  $R^6$  express a hydrogen atom, a halogen atom,  $-NO_2$ ,  $-OH$ , the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced, or the aromatic hydrocarbon group that may be replaced.  $m$  expresses 1, 2, 3, or 4.  $R^7$  expresses the aliphatic hydrocarbon group of a hydrogen atom or the carbon numbers 1-10.  $Z^1$  expresses a hydrogen atom,  $-NH_2$ ,  $-NHR^8$ ,  $-OH$ , or  $-COOH$ .  $n$  expresses 0, 1, or 2.  $R^8$  expresses the aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced.

[0045]As an example (V-1-31) of a compound expressed with said formula (V), what was illustrated to the following table is mentioned suitably. The compound V-6 and  $R^6$  in V-7 mean 3'-Cl, 4'-Cl and 5'-Cl and 6'-Cl.

[0046]

[Table 1]

[0047]

[Table 2]

[0048]Formula (VI)

[0049]

[Formula 18]

[0050]In said formula (VI),  $R^{11}$ ,  $R^{12}$ , and  $R^{13}$  express a hydrogen atom, a halogen atom,  $-NO_2$ ,  $-OH$ , an aliphatic hydrocarbon group of the carbon



numbers 1-10 which may be replaced, or an aromatic hydrocarbon group that may be replaced.  $m$  expresses 1 or 2.  $R^{14}$  and  $R^{15}$  express a hydrogen atom, an aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced, or an aromatic hydrocarbon group that may be replaced.  $X^{1-}$  expresses a counter ion.  $R^{16}$  expresses an aliphatic hydrocarbon group of a hydrogen atom or the carbon numbers 1-10.  $Z^2$  expresses a hydrogen atom,  $-NH_2$ ,  $-NHR^{17}$ ,  $-OH$ , or  $-COOH$ .  $n$  expresses 0, 1, or 2.  $R^{17}$  expresses an aliphatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. However, when all of  $R^{14}$ ,  $R^{15}$ , and  $R^{16}$  are bases other than a hydrogen atom,  $Z^2$  expresses  $-NH_2$ ,  $-NHR^{17}$ ,  $-OH$ , or  $-COOH$ , and  $n$  expresses 1 or 2.

[0051]As an example (VI-1 - 12) of a compound expressed with said formula (VI), what was illustrated to the following table is mentioned suitably.

[0052]

[Table 3]

[0053]Formula (VII)

[0054]

[Formula 19]

[0055]In said formula (VII),  $M^2$  expresses Fe, Ru, or Os.  $X^2$  expresses a halogen atom,  $-OH$ ,  $-CN$ , or  $-SCN$ .  $R^{21} - R^{24}$  express a hydrogen atom, a halogen atom,  $-NO_2$ ,  $-COOH$ ,  $-OH$ ,  $-NH_2$ ,  $-NHR^{25}$ , the aliphatic hydrocarbon group of the carbon numbers 1-10, the aromatic hydrocarbon group that may be replaced, or a heterocycle group.  $R^{25}$  expresses the basis, aliphatic hydrocarbon group, or aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. At least one of  $R^{21} - R^{24}$  expresses  $-COOH$ ,  $-OH$ ,  $-NH_2$ ,  $-NHR^{25}$ , or a pyridyl group.

[0056]As an example (VII-1 - 13) of a compound expressed with said formula (VII), what was illustrated to the following table is mentioned suitably.

[0057]

[Table 4]

[0058]Formula (VIII) [0059]

[Formula 20]

[0060]In said formula (VIII),  $M^3$  expresses Fe, Ru, or Os.  $X^3$  expresses a halogen atom,  $-SO_4$ ,  $-ClO_4$ ,  $-OH$ ,  $-CN$ , or  $-SCN$ .  $n$  expresses 0, 1, or 2.  $R^{31} - R^{36}$  express a hydrogen atom, a halogen atom,  $-NO_2$ ,  $-COOH$ ,  $-OH$ ,  $-NH_2$ ,  $-NHR^8$ , the aliphatic hydrocarbon group of the carbon numbers 1-10, an aromatic hydrocarbon group, or a heterocycle group.  $R^{37}$  expresses the aliphatic hydrocarbon group or aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. At least one of  $R^{31} - R^{36}$  expresses the basis chosen from  $-COOH$ ,  $-OH$ ,  $-NH_2$ ,  $-NHR^{37}$ , or a pyridyl group.

[0061]As an example (VIII-1 - 11) of a compound expressed with said formula (VIII), what was illustrated to the following table is mentioned suitably.

[0062]

[Table 5]

[0063]Formula (IX)

[0064]

[Formula 21]

[0065]In said formula (IX),  $M^4$  expresses Fe, Ru, or Os.  $R^{41} - R^{51}$  express a hydrogen atom, a halogen atom,  $-NO_2$ ,  $-COOH$ ,  $-OH$ ,  $-NH_2$ ,  $-NHR^{53}$ , the aliphatic hydrocarbon group of the carbon numbers 1-10, an aromatic hydrocarbon group, or a heterocycle group.  $R^{53}$  expresses the aliphatic hydrocarbon group or aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. At least one of  $R^{41} - R^{51}$  expresses the basis chosen from  $-COOH$ ,  $-OH$ ,  $-NH_2$ ,  $-NHR^{53}$ , or a pyridyl group.

[0066]As an example (IX-1 - 4) of a compound expressed with said formula (IX), what was illustrated to the following table is mentioned suitably.

[0067]

[Table 6]

[0068]Formula (X)

[0069]

[Formula 22]

[0070]In said formula (X),  $M^5$  expresses (H)<sub>2</sub>, Mg, TiO, VO, Mn, Fe, Co,

nickel, Cu, Zn, GaOH, GaCl, InOH, InCl, or SnO.  $R^{61} - R^{64}$  express a hydrogen atom, a halogen atom,  $-NO_2$ ,  $-NH_2$ ,  $-NHR^{65}$ ,  $-OH$ ,  $-COOH$ , the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced, the aromatic hydrocarbon group that may be replaced, or a heterocycle group. At least one of  $R^{61} - R^{64}$  expresses  $-NH_2$ ,  $-NHR^{65}$ ,  $-OH$ , or  $-COOH$ .  $R^{65}$  expresses the aliphatic hydrocarbon group or aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced. k, l, m, and n express 1 or 2.

[0071]As an example (X-1-15) of a compound expressed with said formula (X), what was illustrated to the following table is mentioned suitably.

[0072]

[Table 7]

[0073]Formula (XI)

[0074]

[Formula 23]

[0075]In said formula (XI),  $M^4$  expresses (H),  $_2$ , Mg, Zn, nickel, Co, Cu, or Pd.  $R^{71} - R^{78}$  express a hydrogen atom, a halogen atom, a hydroxy group, the alkoxy group of the carbon numbers 1-4 which may be replaced, the aliphatic hydrocarbon group of the carbon numbers 1-10 which may be replaced, and the aromatic hydrocarbon group that may be replaced.  $A^1 - A^4$  express the aromatic hydrocarbon group or heterocycle group which may be replaced. At least one of  $A^1 - A^4$  expresses the phenyl group or pyridyl group replaced by  $-NH_2$ ,  $-NHR^{79}$ ,  $-OH$ , or  $-COOH$ .  $R^{79}$  expresses the aliphatic hydrocarbon group or aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced.

[0076]As an example (XI-1 - 6) of a compound expressed with said formula (XI), what was illustrated to the following table is mentioned suitably.

[0077]

[Table 8]

[0078]Formula (XII)

[0079]

[Formula 24]

[0080]In said formula (XII), A<sup>5</sup>, - Express the aromatic hydrocarbon group replaced by the aliphatic hydrocarbon group replaced by NH<sub>2</sub>, -NHR<sup>81</sup>, -OH, -COOH, or a pyridyl group, -NH<sub>2</sub>, -NHR<sup>81</sup>, -OH, -COOH, or a pyridyl group, or a pyridyl group. R<sup>81</sup> expresses the aliphatic hydrocarbon group or aromatic hydrocarbon group of the carbon numbers 1-4 which may be replaced.

[0081]As an example (XII-1 - 19) of a compound expressed with said formula (XII), what was illustrated to the following table is mentioned suitably.

[0082]

[Table 9]

[0083]-- Production of an optical semiconductor electrode -- It can face forming a film chosen from a compound which are said formula (I) - (IV) and is expressed with the surface of said semiconductor material according to a kind at least, and a suitably selected method can be adopted, for example, the following liquid-phase-adsorption methods can be adopted. Make said liquid-phase-adsorption method dip into at least a kind of diluted solution chosen from a compound expressed with said formula (I) - (IV), and said semiconductor material The surface of this semiconductor material, After making Y<sub>1</sub> or a thiol group chosen from a compound expressed with said formula (I) - (IV) react, it is the method of taking out this semiconductor material, washing and drying. [ in / at least / a kind ]

[0084]As a solvent which is chosen from a compound expressed with said formula (I) - (IV) and which dissolves a kind at least, Ester solvent, such as hydrocarbon system solvents, such as toluene, hexane, and hexadecane, and ethyl acetate, Ether system solvents, such as diethylether and a tetrahydrofuran, dichloromethane, Alcoholic solvent, such as ketone solvent, such as halogen system solvents, such as 1,1,2-trichloroethane, acetone, and cyclohexanone, ethanol, and 1-butanol, or these mixed solvents are mentioned. Also in these, what does not react to a compound expressed with said formula (I) - (IV) is preferred, a hydrocarbon system solvent, an ether system solvent, a halogen system solvent, etc. are specifically preferred, and hydrocarbon system solvents, such as toluene, hexane, and hexadecane, are especially preferred.

[0085]Although the concentration of the compound expressed with general formula (I) in said diluted solution - (IV) is usually suitably chosen by 1.0x10<sup>-4</sup>-1.0mol/l., 1.0x10<sup>-4</sup> - especially 1.0x10<sup>-2</sup>mol/l are preferred. Although said reaction may be performed at a room

temperature, in order to promote a reaction, it may carry out in the state where it heated to the temperature below the boiling point if needed, and may carry out by adding a suitable catalyst.

[0086]By a reaction with  $Y_1$  or the thiol group chosen from the compound expressed with the surface, and said formula (I) - (IV) of said semiconductor material in said liquid-phase-adsorption method. [ in / at least / a kind ] Both do a chemical bond and a chemical adsorption film (a chemical-absorption monomolecular film or a chemical-absorption built up film) is formed in the surface of this semiconductor material as the result. And excessive molecules other than said chemical adsorption film adhering to this semiconductor material are washed and removed by said washing.

[0087]For example, as being chosen from the compound expressed with said formula (I) - (IV), using titanium oxide as said semiconductor material, 3-bromopropyl trichlorosilane is used as a kind as it is few, When producing a modified electrode by said liquid-phase-adsorption method, titanium oxide which is a semiconductor material is first immersed in the solution of 3-bromopropyl trichlorosilane. Then, the chemical reaction shown in drawing 1 arises, 3-bromopropyl trichlorosilane carries out a chemical bond to the surface of titanium oxide which is a semiconductor material, and said chemical adsorption film by 3-bromopropyl trichlorosilane is formed in it.

[0088]Under the present circumstances, when it is hard to produce the formation reaction of said chemical adsorption film, catalysts, such as acid and a base, may be added or it may heat. It is also effective in the surface of titanium oxide which is a semiconductor material beforehand by performing heat treatment, acid treatment, plasma treatment, hot water processing, ozonization, etc. to introduce an active layer into the surface of this titanium oxide.

[0089]A method which faces making said chemical adsorption film and coloring matter which were formed as mentioned above react, combining said coloring matter with this chemical adsorption film, and making it fix, and can adopt the suitably selected method, for example, is illustrated below is employable.

[0090]Said halogen atom and the solution of the coloring matter whose functional group in which a reaction is possible is a carboxyl group are made to immerse first the titanium oxide in which said chemical adsorption film was formed in the surface in a primary method. And this chemical adsorption film and the carbo SHIKIRU group in said coloring matter are made to react. Then, the reaction shown in drawing 2 arises, and said coloring matter joins together and is fixed to the surface of this chemical adsorption film. As a result, said coloring

matter is fixed by the surface of titanium oxide which is a semiconductor material via said chemical adsorption film.

[0091] Said halogen atom and the solution of the coloring matter whose functional group in which a reaction is possible is primary amine are made to immerse first the titanium oxide in which said chemical adsorption film was formed in the surface in the second method. And this chemical adsorption film and the carbo SHIKIRU group in said coloring matter are made to react. Then, the reaction shown in drawing 3 arises, and said coloring matter joins together and is fixed to the surface of this chemical adsorption film. As a result, said coloring matter is fixed by the surface of titanium oxide which is a semiconductor material via said chemical adsorption film.

[0092] As a solvent used when preparing the solution of said coloring matter, For example, ester solvent, such as hydrocarbon system solvents, such as toluene, hexane, and hexadecane, and ethyl acetate, Ether system solvents, such as diethylether and a tetrahydrofuran, dichloromethane, Amide system solvents, such as alcoholic solvent, such as ketone solvent, such as halogen system solvents, such as 1,1 and 2-trichloroethane, acetone, and cyclohexanone, ethanol, and 1-butanol, N.N-dimethylformamide, and N-methyl pyrrolidone, or these mixed solvents are mentioned. Also in these, it is said general formula. It has sufficient solubility to the compound expressed with (V) - (XII), And the formed chemical adsorption film and said general formula What does not react to the compound expressed with (I) - (IV) in itself is preferred, Polar aprotic solvents, such as halogen system solvents, such as ether system solvents, such as hydrocarbon system solvents, such as toluene, and a tetrahydrofuran, and dichloromethane, and N.N-dimethylformamide, etc. are preferred.

[0093] The semiconductor electrode produced by making it above can absorb sunlight efficiently, can perform energy conversion, is excellent in photoelectric conversion efficiency, stability, and endurance, is easy to manufacture and can be used conveniently for the photoelectric conversion method of this invention and photoelectric conversion device which are mentioned later.

[0094] (A photoelectric conversion device and the photoelectric conversion method) In the photoelectric conversion method of this invention, the electrode of the couple which was mutually connected so that energization was possible, and has been arranged in an electrolytic solution is irradiated, and a photoelectric conversion reaction is produced. At least one side of the electrodes of this couple in said photoelectric conversion method is an optical semiconductor electrode of said this invention, and other one side is

counterelectrodes. The photoelectric conversion method of this invention can be suitably enforced using the photoelectric conversion device of this invention. The photoelectric conversion device of this invention has a means to connect the electrode of the couple arranged in an electrolytic solution, and the electrode of this couple so that energization is possible, at least one side of the electrodes of this couple is an optical semiconductor electrode of said this invention, and other one side is counterelectrodes.

[0095]- Counterelectrode - as the optical semiconductor electrode (it may be called a "modified electrode") of said this invention, and a counterelectrode used for a pair, Oxidize and it can be hard to be returned, and if stable, lessons will be taken from the material, shape, structure, a size, etc., and restriction in particular is not, and it can choose suitably, for example, can choose from transparent electrodes, such as charges of a plate, such as palladium and black lead, ITO glass, and Nesa glass, etc.

[0096]-A means to connect a pair of electrodes so that energization is possible - as a means to connect the electrode of the couple by said optical semiconductor electrode (modified electrode) and said counterelectrode so that energization is possible, A wire rod, a plate, a printed film, a vacuum evaporation film, etc. which restriction in particular does not have, and can choose suitably according to the purpose, for example, consist of conductive materials, such as a publicly known lead or various metal, carbon, and a metallic oxide, in itself are mentioned suitably.

[0097]- Electrolytic solution - As said electrolytic solution, there is no restriction in particular and it can choose suitably, For example, salts, such as sodium sulfate, potassium chloride, a lithium chloride, and tetraethylammonium perchlorate, Nonaqueous solvents, such as acids, such as alkali, such as sodium hydroxide and potassium carbonate, sulfuric acid, and chloride, solution of the mixture of this, alcohols, and propylene carbonate, etc. can be used. In this invention, the substance in which it is the purpose of planning stability of the photoelectric current characteristic, and also potassium iodide, p-benzoquinone, etc. produce oxidation and a reduction reaction reversibly may be added in proper quantity in said electrolysis room solution.

[0098]- In the photoelectric conversion device and the photoelectric conversion method of photoelectric conversion reaction-this invention, a photoelectric conversion reaction can be produced as follows. That is, the above-mentioned electrode (modified electrode), i.e., said optical semiconductor electrode, and said counterelectrode of a couple

are first immersed into said nature solution of an electric field. Next, monochromatic light which is equivalent to a 300-400-nm ultraviolet area thru/or the absorption wavelength region of the coloring matter made to fix on a semiconductor electrode to said semiconductor electrode, multicolor light which includes one of the zones, Or if it irradiates with white light thru/or multicolor lights, such as sunlight, light energy will be transformed into electrical energy, or hydrogen will occur simultaneously in the electrode surface by the side of a cathode, and oxygen will occur in the electrode surface by the side of an anode.

[0099]In this invention, since the electrode of a special couple mentioned above is used, in addition to the ultraviolet radiation in sunlight, even visible light or a near infrared is efficiently used for a photoelectric conversion reaction, and light energy can be transformed into chemical energy or electrical energy. As a result, synthetic use of lights, such as sunlight, is attained and effective use of light energies, such as sunlight, is attained at high efficiency. And in said optical semiconductor electrode (modified electrode) to be used, Since coloring matter has combined with the surface firmly by the covalent bond and it is not easily desorbed from this optical semiconductor electrode (modified electrode), the characteristic of this optical semiconductor electrode (modified electrode) is stabilized for a long period of time, can be maintained, and can always perform a photoelectric conversion reaction efficiently.

[0100]

[Example]Although the example of this invention is described below, this invention is not limited to these examples at all.

(Example 1)

- It added gradually, agitating violently 25 ml of preparation-alt.titanic acid-tetra-\*\*\*\*- propyl of a titanium oxide colloidal solution to the mixed solution of 150 ml of distilled deionized water, and the concentrated nitric acid 1.54g (specific gravity: 1.38). Temperature up was carried out to 80 \*\*, continuing churning, and it held, continuing churning for 8 hours. All the above operations were performed under the dry nitrogen air current. In this way, the milky stable titanium oxide colloidal solution was obtained. Using the rotating evaporator, this colloidal solution was condensed until 40 ml of viscous liquids remained under decompression of 30 \*\* and 30mmHg.

[0101]- Production of an optical semiconductor electrode (modified electrode) - After coating said titanium oxide colloidal solution with a spin coat method on an ITO glass substrate, it was calcinated at 500



\*\* for 1 hour. The thickness of the semiconductor membrane by the titanium oxide formed on the ITO glass substrate was about 0.3 micrometer. When the structure of the obtained semiconductor membrane was investigated with the X-ray diffraction method, it was a mixture of ANATASU and rutile. By the above, ITO / titanium oxide composite material was obtained. It decided to use this as a substrate. Next, the content of 3-bromopropyl trichlorosilane made said ITO / titanium oxide composite material immersed to the mixed solvent (capacity factor 4:1) of n-hexadecane and a carbon tetrachloride for 2 hours into the solution which is  $10^{-3}$ mol/l. Then, after having taken out this ITO / titanium oxide composite material out of said solution, fully washing using n-hexadecane and acetone and carrying out natural seasoning for 30 minutes under a nitrogen atmosphere, it heated for 30 minutes at 80 \*\*.

[0102]Business of the surface of ITO / titanium oxide composite material processed as mentioned above was carried out, and X linear-light electronic spectral device (the product made by VG: ESCALAB-220i) was observed for it. The measurement result of X-ray photoelectron spectroscopy was shown in drawing 4. In the data shown in drawing 4, near 70 eV, near 180 eV, and near 256 eV, 3 d of Br atom, The signal from 3p and 3s was observed, respectively, and it was checked that 3-bromopropyl trichlorosilane has combined with the titania film currently formed in the surface of ITO / titanium oxide composite material.

[0103]ITO / titanium oxide composite material which 3-bromopropyl trichlorosilane combined with the surface, It was immersed in the dimethylformamide solution (concentration:  $5 \times 10^{-4}$ mol/l) of 4-carboxy-2',4',5',7'-tetraiodofluorescein (said compound (V-8)), and was made to react at 90 \*\* for 24 hours. ITO / titanium oxide composite material which 3-bromopropyl trichlorosilane combined with the surface using ethanol and acetone were fully washed after ending reaction, and natural seasoning was carried out for 30 minutes under a nitrogen atmosphere. The optical semiconductor electrode (modified electrode) of Example 1 was produced as mentioned above.

[0104]The obtained optical semiconductor electrode (modified electrode) was assuming light pink, and was transparent. The surface of this optical semiconductor electrode (modified electrode) was observed by X-ray photoelectron spectroscopy. The measurement result of X-ray photoelectron spectroscopy was shown in drawing 5. In the data shown in drawing 5, the signals of Br atom near 70 eV, near 180 eV, and near 256 eV decrease in number, The signal from each 3p<sub>1/2</sub> of I atom of 4-carboxy-2',2',5',7'-tetraiodofluorescein, 3p<sub>3/2</sub>, three p<sub>5</sub>

/ 2 or 4d was observed instead near 930 eV, near 874 eV, near 630 eV, near 620 eV, and near 50 eV.

[0105]When the ultraviolet and visible absorption spectrum was measured, it was the almost same spectral shape as the ethanol solution of 4-carboxy-2',2',5',7'-tetraiodofluorescein. The ultraviolet visible absorption spectrum of the obtained sample was shown in drawing 6. It was checked that 4-carboxy-2',4',5',7'-tetraiodofluorescein is fixed on a titanium oxide layer from the data of drawing 6 via the chemical adsorption film which consists of 3-bromopropyl trichlorosilane. By the above, the optical semiconductor electrode 1 as shown in drawing 7 was produced. the optical semiconductor electrode 1 shown in drawing 7 -- the glass base material 2 top -- the ITO layer 3 and the titanium oxide layer 4 -- and, Having the pigment layer 5 by 3-bromopropyl trichlorosilane and 4-carboxy-2',2',5',7'-tetraiodofluorescein in this order, these lamination sides were covered with the epoxy resin as the adhesive agent 6, and have adhered. It is connected to a part of ITO layer 3 in the state which can energize the lead 7.

This lead 7 is accommodated in the glass tube 8.

[0106]The electrode of the couple by the produced optical semiconductor electrode and the platinum electrode selected as a counterelectrode was connected with the lead used as a means to connect so that energization of the electrode of this couple is possible. The photoelectric conversion device which consists of a lead which connects the electrode of a couple and the electrode of this couple as mentioned above was produced. This photoelectric conversion device was used as the photoelectric conversion device of Example 1.

[0107] (Measurement of photoelectric current) Measurement of photoelectric current was performed as follows using the above-mentioned photoelectric conversion device. That is, as shown in drawing 8, the electrode 1, i.e., the optical semiconductor electrode, and the counterelectrode 9 of the couple were immersed into the electrolytic solution 11. Said electrolytic solution 11 is solution which adds sodium sulfate by 0.1 mol/l and adds potassium iodide at a rate of 0.02 mol/l as an electrolyte to the distilled deionized water. As shown in drawing 8, the photoelectric conversion device was constituted in the potentiostat here, and also the saturated calomel electrode was used as the reference electrode 10.

[0108]The photoelectric current-time response curve when the potential of said optical semiconductor electrode (modified electrode) was held to 0V (vs S C E) and irradiated with white light (the xenon lamp of

500W, illumination 4000lux) was shown in drawing 9 (left-hand side data). The result when the semiconductor electrode which consists only of titanium oxide which is not fixing coloring matter was used as said optical semiconductor electrode (modified electrode) (the below-mentioned comparative example 1) was also shown in drawing 9 (right-hand side data).

[0109] The photoelectric current-time response curve when the potential of said optical semiconductor electrode (modified electrode) was held to 0V (vs S C E) and irradiated with 550-nm monochromatic light (1 mW/cm<sup>2</sup>) was shown in drawing 10 (left-hand side data). It is clear that photoelectric current will increase from this data compared with the case (the below-mentioned comparative example 1) where coloring matter is not being fixed if coloring matter is being fixed to the modified electrode (photoelectrical pole) (data on the right-hand side of drawing 10). Under the present circumstances, it was checked that gas is emitted from the surface of said optical semiconductor electrode (modified electrode). When it did not irradiate with light, inter-electrode bias voltage was set to 0V and current irradiated with light to hardly flowing, current was observed as for 0V in inter-electrode bias voltage. If this is used [said optical semiconductor electrode (modified electrode)], even if it will not impress external bias voltage, it shows that the photolysis of the water is carried out. After holding the potential of the optical semiconductor electrode (modified electrode) to 0V (vs S C E) and irradiating with white light (the xenon lamp of 500W, illumination 4000lux) for 1 consecutive hour, the photoelectric current-time response curve was measured. The result was shown in Table 10.

[0110] (Example 2) In Example 1, it is rhodamine 6G about 4-carboxy-2',4',5',7'-tetraiodofluorescein (said compound (V-8)). (said compound (VI-7)) Outside replaced with is made to be the same as that of Example 1, The optical semiconductor electrode (modified electrode) was produced and the photoelectric conversion device of Example 2 was produced. Photoelectric current as well as Example 1 was measured using the photoelectric conversion device of Example 2. The result was shown in Table 10.

[0111] (Example 3) In Example 1, It is bis(2,2'-bipyridine 4,4-dicarboxylic acid)ruthenium (II) dithiocyanate about 4-carboxy-2',4',5',7'-tetraiodofluorescein (said compound (V-8)). (said compound (VII-7)) Outside replaced with is made to be the same as that of Example 1, The optical semiconductor electrode (modified electrode) was produced and the photoelectric conversion device of Example 3 was produced. Photoelectric current as well as Example 1 was measured

using the photoelectric conversion device of Example 3. The result was shown in Table 10.

[0112](Example 4) In Example 1, It is bis(2,2'-bipyridine)(2,2'-bipyridine 4,4-dicarboxylic acid) ruthenium (II) JIJKURORIDO about 4-carboxy-2',4',5',7'-tetraiodofluorescein (said compound (V-8)). (said compound (VIII.)) -Like Example 1, the outside replaced with 5 produced the optical semiconductor electrode (modified electrode), and produced the photoelectric conversion device of Example 4.

Photoelectric current as well as Example 1 was measured using the photoelectric conversion device of Example 4. The result was shown in Table 10.

[0113](Example 5) In Example 1, outside which replaced 4-carboxy-2',4',5',7'-tetraiodofluorescein (said compound (V-8)) with the tetra(n-butyl) ammonium salt of said compound (IX-1) is made to be the same as that of Example 1, The optical semiconductor electrode (modified electrode) was produced and the photoelectric conversion device of Example 5 was produced. Photoelectric current as well as Example 1 was measured using the photoelectric conversion device of Example 5. The result was shown in Table 10.

[0114](Example 6) In Example 1, outside which replaced 4-carboxy-2',4',5',7'-tetraiodofluorescein (said compound (V-8)) with cobalt (tetracarboxy phthalocyaninato) (II) (said compound (X-9)) is made to be the same as that of Example 1, The optical semiconductor electrode (modified electrode) was produced and the photoelectric conversion device of Example 6 was produced. Photoelectric current as well as Example 1 was measured using the photoelectric conversion device of Example 6. The result was shown in Table 10.

[0115](Example 7) In Example 1, They are meso-porphyrin 4,4',4'' and 4'''-tetrabenzoic acid about 4-carboxy-2',4',5',7'-tetraiodofluorescein (said compound (V-8)). (said compound (XI-1)) Outside replaced with is made to be the same as that of Example 1, The optical semiconductor electrode (modified electrode) was produced and the photoelectric conversion device of Example 7 was produced. Photoelectric current as well as Example 1 was measured using the photoelectric conversion device of Example 7. The result was shown in Table 10.

[0116](Example 8) In Example 1, It is (4,4',4'' and 4'''-tetra pyridyl)-meso-porphyrin about 4-carboxy-2',4',5',7'-tetraiodofluorescein (said compound (V-8)). (said compound (XI-6)) Outside replaced with is made to be the same as that of Example 1, The optical semiconductor electrode (modified electrode) was produced and the photoelectric conversion device of Example 8 was produced. Photoelectric current as well as Example 1 was measured using the photoelectric conversion

device of Example 8. The result was shown in Table 10.

[0117] (Example 9) In Example 1, it is 4-carboxy-2',4',5',7'-tetraiodofluorescein (said compound (V-8)) (the outside replaced with N,N'-bis(2-carboxyethyl)perylene diimide (said compound (XII-2)) like Example 1). The optical semiconductor electrode (modified electrode) was produced and the photoelectric conversion device of Example 9 was produced. Photoelectric current as well as Example 1 was measured using the photoelectric conversion device of Example 9. The result was shown in Table 10.

[0118] (Example 10) In Example 1, it is 4-carboxy-2',4',5',7'-tetraiodofluorescein (the outside which replaced with said compound (V-8), and used 4-amino-fluorescein (V-20)). The optical semiconductor electrode (modified electrode) was produced like Example 1, and the photoelectric conversion device of Example 10 was produced. The obtained optical semiconductor electrode (modified electrode) was assuming light pink, and was transparent. When the ultraviolet and visible absorption spectrum of this optical semiconductor electrode (modified electrode) was measured, it was the almost same spectral shape as the ethanol solution of 4-amino-fluorescein. Photoelectric current as well as Example 1 was measured using the photoelectric conversion device of Example 10. The result was shown in Table 10.

[0119] (Example 11) In Example 1, the outside which replaced with 3-bromopropyl trichlorosilane and used 8-bromooctyltrichlorosilane produced the optical semiconductor electrode (modified electrode) like Example 1, and produced the photoelectric conversion device of Example 11. Photoelectric current as well as Example 1 was measured using the photoelectric conversion device of Example 11. The result was shown in Table 10.

[0120] (Example 12) In Example 1, the outside which replaced with 3-bromopropyl trichlorosilane and used 3-chloropropyl methyldiethoxysilane produced the optical semiconductor electrode (modified electrode) like Example 1, and produced the photoelectrolysis device of Example 12. Photoelectric current as well as Example 1 was measured using the photoelectric conversion device of Example 12. The result was shown in Table 10.

[0121] (Example 13) In Example 1, the outside which replaced with 3-bromopropyl trichlorosilane and used 8-bromooctyldimethylchlorosilane produced the optical semiconductor electrode (modified electrode) like Example 1, and produced the photoelectric conversion device of Example 13. Photoelectric current as well as Example 1 was measured using the photoelectric conversion device of Example 13. The result was shown in Table 10.

[0122](Example 14) In Example 1, the outside which replaced with 3-bromopropyl trichlorosilane and used 3-bromopropyl trichloro germane produced the optical semiconductor electrode (modified electrode) like Example 1, and produced the photoelectric conversion device of Example 14. Photoelectric current as well as Example 1 was measured using the photoelectric conversion device of Example 14. The result was shown in Table 10.

[0123](Comparative example 1) In Example 1, the outside which did not have \*\* for 3-bromopropyl trichlorosilane and 4-carboxy-2',4',5',7'-tetraiodofluoresceins produced the modified electrode like Example 1, and produced the photoelectric conversion device of the comparative example 1. Photoelectric current as well as Example 1 was measured using the photoelectric conversion device of the comparative example 1. The result was shown in Table 10.

[0124](Comparative example 2) After forming titanium oxide semiconductor membrane on an ITO glass substrate in Example 1, No chemical-absorption processing by 3-bromopropyl trichlorosilane is performed, The outside which immersed ITO / titanium oxide composite material in the ethanol solution (concentration:  $10^{-3}$  mol/l) of 4-carboxy-2',4',5',7'-tetraiodofluorescein (said compound (V-8)) for 8 hours, The modified electrode was produced like Example 1 and the photoelectric conversion device of the comparative example 2 was produced. When the ultraviolet and visible absorption spectrum of the modified electrode of the comparative example 2 was measured, it was the almost same spectral shape as the ethanol solution of 4-carboxy-2',2',5',7'-tetraiodofluorescein. Photoelectric current as well as Example 1 was measured using the photoelectric conversion device of the comparative example 2. The result was shown in Table 10.

[0125](Comparative example 3) In Example 1, after forming titanium oxide semiconductor membrane on an ITO glass substrate, the outside which replaced with 3-bromopropyl trichlorosilane and used gamma-aminopropyl triethoxysilane produced the modified electrode like Example 1, and produced the photoelectric conversion device of the comparative example 3. Photoelectric current as well as Example 1 was measured using the photoelectric conversion device of the comparative example 3. The result was shown in Table 10.

[0126]

[Table 10]

[0127]

[Effect of the Invention]According to this invention, many problems in

said former can be solved, sunlight can be absorbed efficiently, and energy conversion can be performed, It excels in photoelectric conversion efficiency, stability, and endurance, and a suitable photoelectric conversion device to enforce the photoelectric conversion method using an optical semiconductor electrode with easy manufacture and this optical semiconductor electrode and this photoelectric conversion method can be provided.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1]Drawing 1 is a conceptual enlarged drawing for explaining an example in the state where the chemical adsorption film was formed on the surface of the semiconductor material.

[Drawing 2]Drawing 2 is a conceptual enlarged drawing for explaining an example in the state where coloring matter was fixed via the chemical adsorption film on the surface of the semiconductor material.

[Drawing 3]Drawing 3 is a conceptual enlarged drawing for explaining an example in the state where coloring matter was fixed via the chemical adsorption film on the surface of the semiconductor material.

[Drawing 4]Drawing 4 is data in which X linear-light electronic part light spectrum of the surface of this semiconductor material after combining 3-bromopropyl trichlorosilane with the surface of ITO / titanium oxide composite material as a semiconductor material is shown.

[Drawing 5]Drawing 5 on the surface of ITO / titanium oxide composite material as a semiconductor material which 3-bromopropyl trichlorosilane combined. It is data in which X linear-light electronic part light spectrum of the surface of this semiconductor material after combining 4-carboxy-2',4',5',7'-tetraiodofluorescein is shown.

[Drawing 6]Drawing 6 is data in which the ultraviolet and visible absorption spectrum of the modified electrode in Example 1 is shown.

[Drawing 7]Drawing 7 is a section approximate account figure of the modified electrode in Example 1.

[Drawing 8]Drawing 8 is an approximate account figure of the photoelectrolysis device of Example 1.

[Drawing 9]Drawing 9 shows the current-time curve at the time of the white light exposure to a modified electrode [ in / in left-hand side data / Example 1 ], and shows the current-time curve at the time of

the white light exposure to a modified electrode [ in / in right-hand side data / the comparative example 1 ].

[Drawing 10]Drawing 10 shows the current-time curve at the time of the monochromatic light (550 nm) exposure to a modified electrode [ in / in left-hand side data / Example 1 ], and shows the current-time curve at the time of the monochromatic light (550 nm) exposure to a modified electrode [ in / in right-hand side data / the comparative example 1 ].

[Drawing 11]Drawing 11 is data in which the ultraviolet and visible absorption spectrum of the modified electrode in the comparative example 2 is shown.

[Description of Notations]

- 1 Optical semiconductor electrode (modified electrode)
  - 2 Glass base material
  - 3 ITO layer
  - 4 Titanium oxide layer
  - 5 Pigment layer
  - 6 Adhesive agent
  - 7 Lead
  - 8 Glass tube
  - 9 Counterelectrode
  - 10 Contrast electrode
  - 11 Electrolytic solution
  - 12 Potentiostat
-